THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

Project 3143

Report One

A Progress Report

to

MEMBERS OF GROUP PROJECT 3143

December 5, 1973

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SUMMARY

This report covers the preparation and characterization of the polymers, particles, and pulp fibers which will be the subject materials for this investigation.

Five samples of sodium polystyrenesulfonate with narrow molecular weight distribution have been synthesized for use as the model polymer flocculant. The molecular weights range from 73,000 to 4 million. Intrinsic viscosity, sedimentation equilibrium, and carbon-sulfur elemental analyses indicate that no chain degradation or cross-linking has occurred during the synthesis and that sulfonation is complete. Potentiometric titration results show that the polymer is more than 90% neutralized at any pH greater than 4 when the ionic strength is between zero and 0.55. Commercial samples of sodium polystyrenesulfonate have been obtained for the large-scale studies. An ultraviolet spectroscopy method has been developed to determine the amount of polymer left in solution subsequent to its adsorption onto the particle surface. It is felt that a well-characterized set of polymer samples has been produced.

Titanium dioxide suspensions with well-defined particle size distribution and specific surface area have been prepared. These will be the particles used in the flocculation and retention studies. A large batch of bleached softwood kraft pulp was beaten to 400 CF for subsequent use in the retention experiments. The necessary materials for the remainder of the program have been prepared.

The ongoing and proposed future work on the project is detailed. The most important parameter whose effect needs to be understood is that of agitation both during and following floc formation.

INTRODUCTION

This progress report covers the background work of preparing and characterizing the materials to be used in the balance of the program. The primary goal of this project is to gain a better understanding of the flocculation and retention process at the molecular level. This understanding, we believe, is necessary to effect any real improvement in actual commercial processes. To facilitate our reaching the objectives, care and time have been taken to obtain well-defined materials with which to perform the experiments.

MODEL POLYMERS

One of the goals of this project is to ascertain the effect of the molecular weight of the flocculation aid on floc formation and stability. To achieve this unambiguously requires the use of narrow fractions of the polymer. With the usual commercial polymers having broad molecular weight distributions, it is not possible to determine which molecular weight species are responsible for the flocculation behavior observed. The use by other workers of such polymers with molecular weight heterogeneity probably accounts in part for the conflicting conclusions found in the literature (1-4) concerning the effect of molecular weight. There are in general two methods to obtain the polymer fractions. The first is by fractionation of the usual broad molecular weight distribution material. The common techniques are fractional precipitation and gel permeation chromatography. Either requires that the resulting fractions be characterized with respect to molecular weight and molecular weight heterogeneity. The other method is to use a special synthesis which leads to a polymer with a narrow molecular weight distribution. The "living polymer" technique developed by Szwarc (5) and his school results in a product with $\langle M \rangle_w / \langle M \rangle_n$ (ratio of weight to number average molecular weights) of 1.1 or less. Commercial polymers usually are characterized by $\langle M \rangle_w / \langle M \rangle_n$ of 2 or 3 or more. In this project the second route to narrow fractions was used.

SYNTHESIS

Sodium polystyrenesulfonate (NaPSS) was chosen as the model polymer because it can be prepared with known molecular weight distribution. The synthesis is a two step process. First, styrene is polymerized by the "living polymer" technique (5). Then the polystyrene is sulfonated in a manner that

produces no chain length degradation or cross-linking and results in 100% sulfonation. Such a procedure has been described by Carroll and Eisenberg (6). Because the reaction is "clean," the molecular weight of the sulfonated material can be calculated from that of the polystyrene if the latter is known.

Five samples of polystyrene produced by the "living polymer" technique were purchased (Pressure Chemical Co., Pittsburgh, Pa.). The molecular weight and heterogeneity index as supplied by the manufacturer (measured at the Mellon Institute) are listed in Table I.

TABLE I

CHARACTERIZATION OF POLYSTYRENES

Sample	$\langle M \rangle_w$ (x 10^{-3})	$\langle M \rangle_w / \langle M \rangle_n$
PCC 7b	37	$\leq$1.06
PCC 4b	110	$\leq$1.06
PCC 1c	200	$\leq$1.06
PCC 13a	670	$\leq$1.10
PCC 14b	2050	$\leq$1.30

These samples were sulfonated as prescribed by Carroll and Eisenberg (6). The polystyrene was reacted with 100% sulfuric acid with Ag_2SO_4 present to prevent sulfone formation and the consequent cross-linking. The reaction proceeds rapidly at room temperature to give almost quantitative yields of polystyrenesulfonic acid (PSSA). The products were dialyzed exhaustively to remove unreacted H_2SO_4 and the Ag^+. Because the acid form is unstable (6,7), the sodium salt was prepared by titrating the dialyzed PSSA with NaOH to a pH of 7. These potentiometric titrations also served to characterize the degree of neutralization as a function of pH (see below). The neutralized polymer

was concentrated on an Amicon Ultrafiltration Apparatus and subsequently freeze dried. The carefully dried samples were weighed and then allowed to equilibrate under constant conditions of 72°F and 50% RH. The extremely hygroscopic polymer contained about 15% water under these conditions.

CHARACTERIZATION

Although it is possible to calculate the molecular weight of the NaPSS from the known molecular weight of the polystyrene samples (6,7), it was considered necessary to make checks for the possibility of incomplete sulfonation or chain degradation. The intrinsic viscosities of the NaPSS samples were determined at 30°C in 0.5M NaCl to suppress the ionic intramolecular repulsion effects. The results are shown in Fig. 1 as the logarithm of the intrinsic viscosity $[\eta]$ plotted against the logarithm of the molecular weight. The latter were calculated from the values of the polystyrene starting materials listed in Table I by multiplication by the ratio of the monomer molecular weights of the two materials (1.98). The results fall satisfactorily about a straight line which can be expressed as the following equation with $[\eta]$ in units of ml/g.

$$[\eta] = 1.46 \times 10^{-2} M^{0.67}$$

The dashed line in Fig. 1 represents the results of Nagasawa and coworkers (8) for the same polymer and salt system at 25°C.

$$[\eta] = 1.86 \times 10^{-2} M^{0.64}$$

The slightly greater magnitudes of the intrinsic viscosities in the present results and the larger exponent on the molecular weight can be attributed to the 0.5M NaCl-H_2O system being a better solvent in the thermodynamic sense at the higher temperature. This is the expected result for most polymer systems

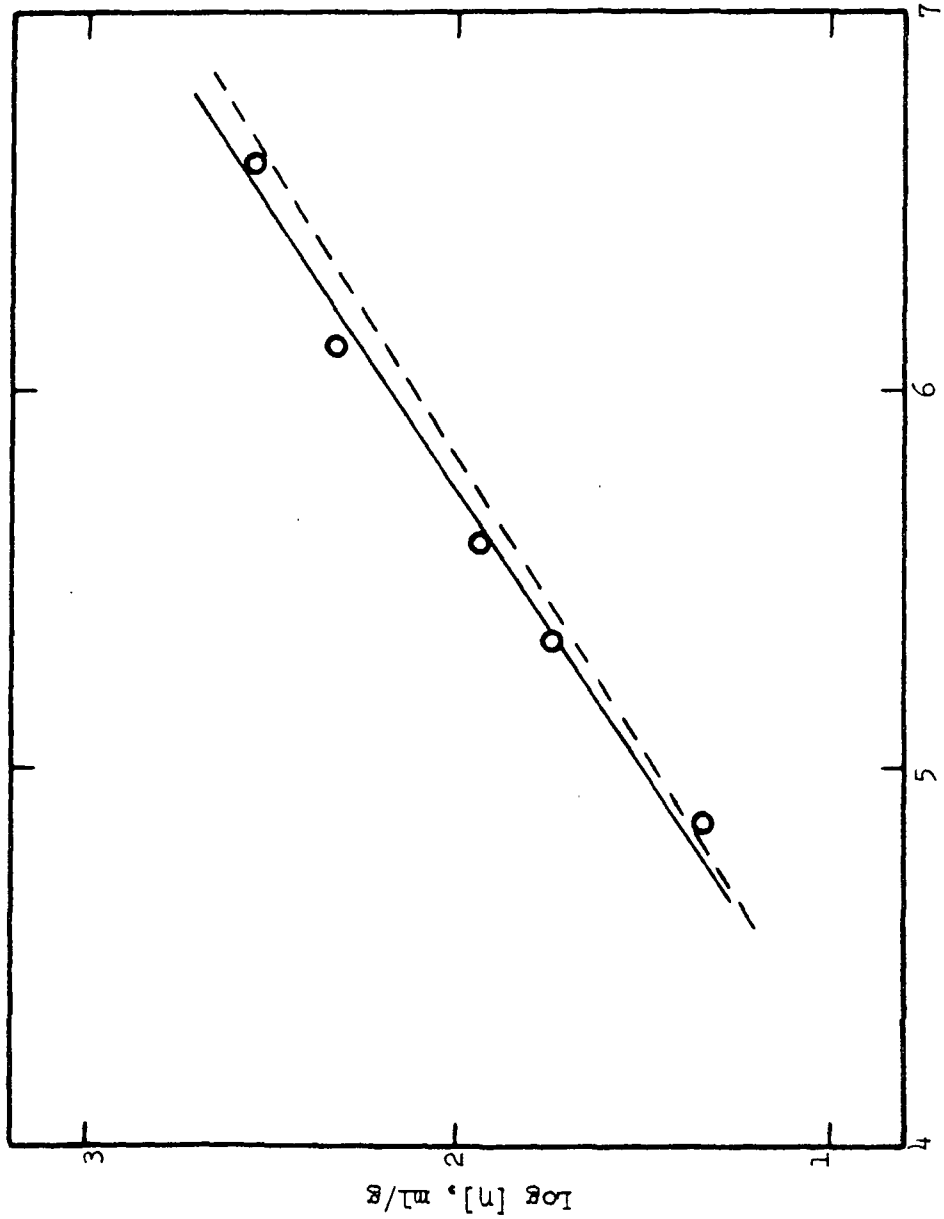

Figure 1. Dependence of Intrinsic Viscosity of NaPSS in 0.5M NaCl-H_2O on Molecular Weight. Solid Line: Best Fit to Data Points at 30°C. Dashed Line: Results of Takahashi, et al. (8) at 25°C

and is borne out by the data on the variation of the intrinsic viscosity with temperature of the potassium salt of PSSA in KCl-H_2O solution (6). The conclusion is that the molecular weights of the sulfonated polystyrenes are those calculated from the values of the polystyrene starting materials.

As a further check on this point the molecular weight of the sample from PCC 4b was determined by a sedimentation equilibrium experiment in the analytical ultracentrifuge. A 0.025% solution of the NaPSS sample in 0.5M NaCl-H_2O solvent was run at 12,545 rpm at 30°C. The molecular weight found was 212,000 compared to a calculated value of 218,000. The excellent agreement shows that sulfonation was complete and that no cross-linking or chain degradation occurred during the synthesis and workup.

The new designations and calculated molecular weights of the synthesized samples are given in Table II.

TABLE II

CHARACTERIZATION OF SODIUM POLYSTYRENESULFONATES

Sample	$\langle M \rangle_w \times 10^{-3}$
A. Synthesized materials	
S-73	73
S-218	218
S-396	396
S-1330	1330
S-3960	3960
B. Commercial materials	
V-70	70
V-500	500
V-700	7000

Carbon and sulfur elemental analyses were carried out on Sample S-218. An uncertain amount of water present in the sample negated absolute values of the carbon and sulfur contents from being determined. However, the ratio of % S/% C was found to be 0.334, identical to that calculated. This result lends further support to the assumption that 100% sulfonation of the polystyrenes was produced.

As mentioned previously, the sodium salts of the PSSA samples were obtained by potentiometric titration of the polyacids to neutrality. This procedure also allowed a determination of the dependence of the degree of neutralization on pH and the variation of this dependence with molecular weight. The neutralizations were carried out in a stirred cell by using 0.1N NaOH as the titrant. The results are presented in Fig. 2 where the pH is plotted against a function ΔV of the amount of titrant added. Here ΔV is the milliequivalents of titrant at pH equal to 7 minus the milliequivalents of titrant at the pH on the ordinate. In other words, it is equal to the milliequivalents of polymer that are not neutralized at a given pH. All of the data for the samples with different molecular weights fall along a single smooth curve. From this result it can be concluded that the degree of neutralization at a given pH is independent of the molecular weight. This is a finding common to most polyelectrolytes (9).

The effect of ionic strength on the degree of neutralization at a given pH was determined by carrying out careful titrations of a sample of S-218. These were performed with the solution under a blanket of nitrogen to prevent CO_2 absorption by the solution. A typical set of data is shown in Fig. 3. Here the pH is plotted against the amount of base added for the case with no added salt. As would be expected for a strong acid, the curve shows a single sharp break with

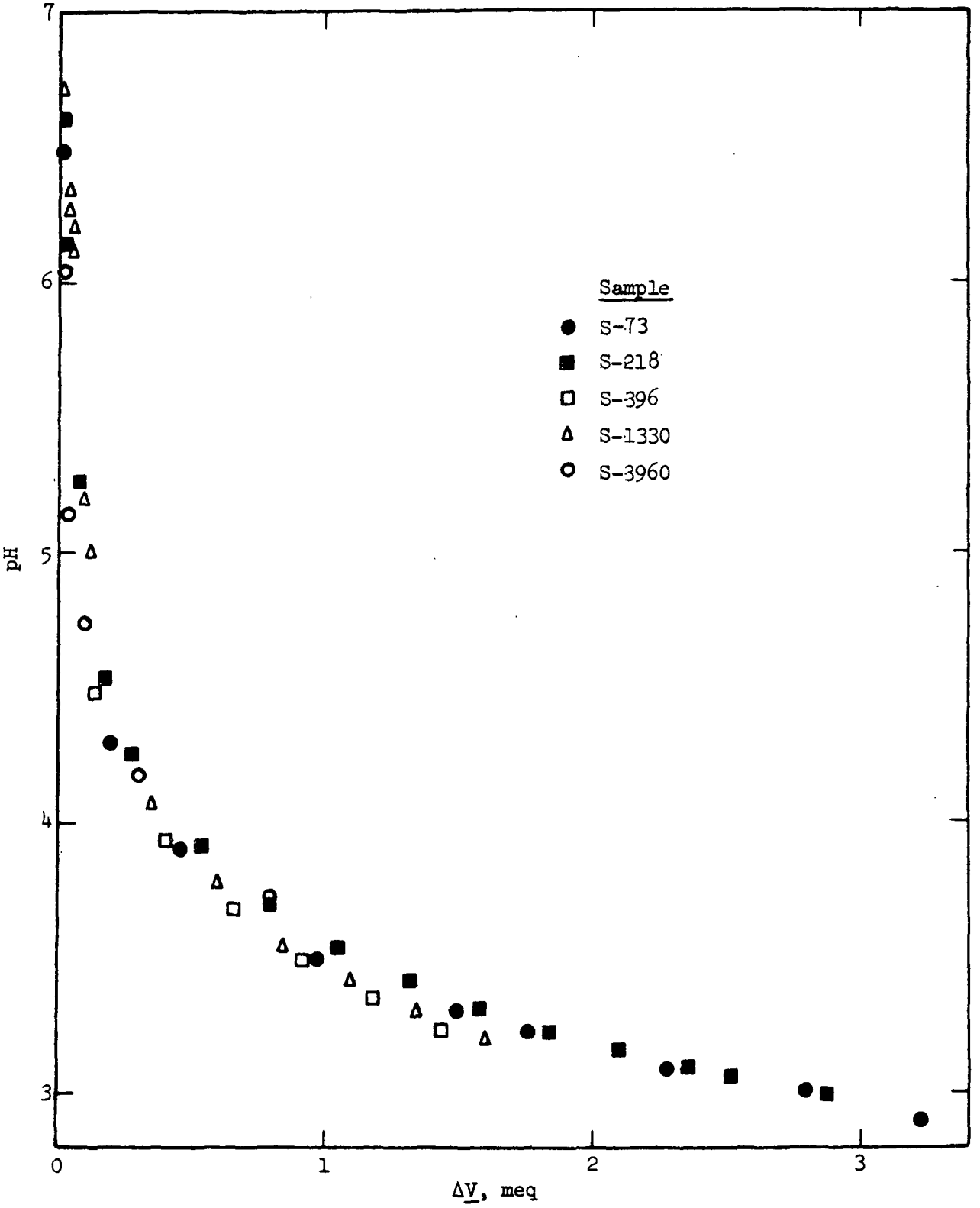

Figure 2. Dependence of pH on Displacement from Neutrality as a Function of Molecular Weight

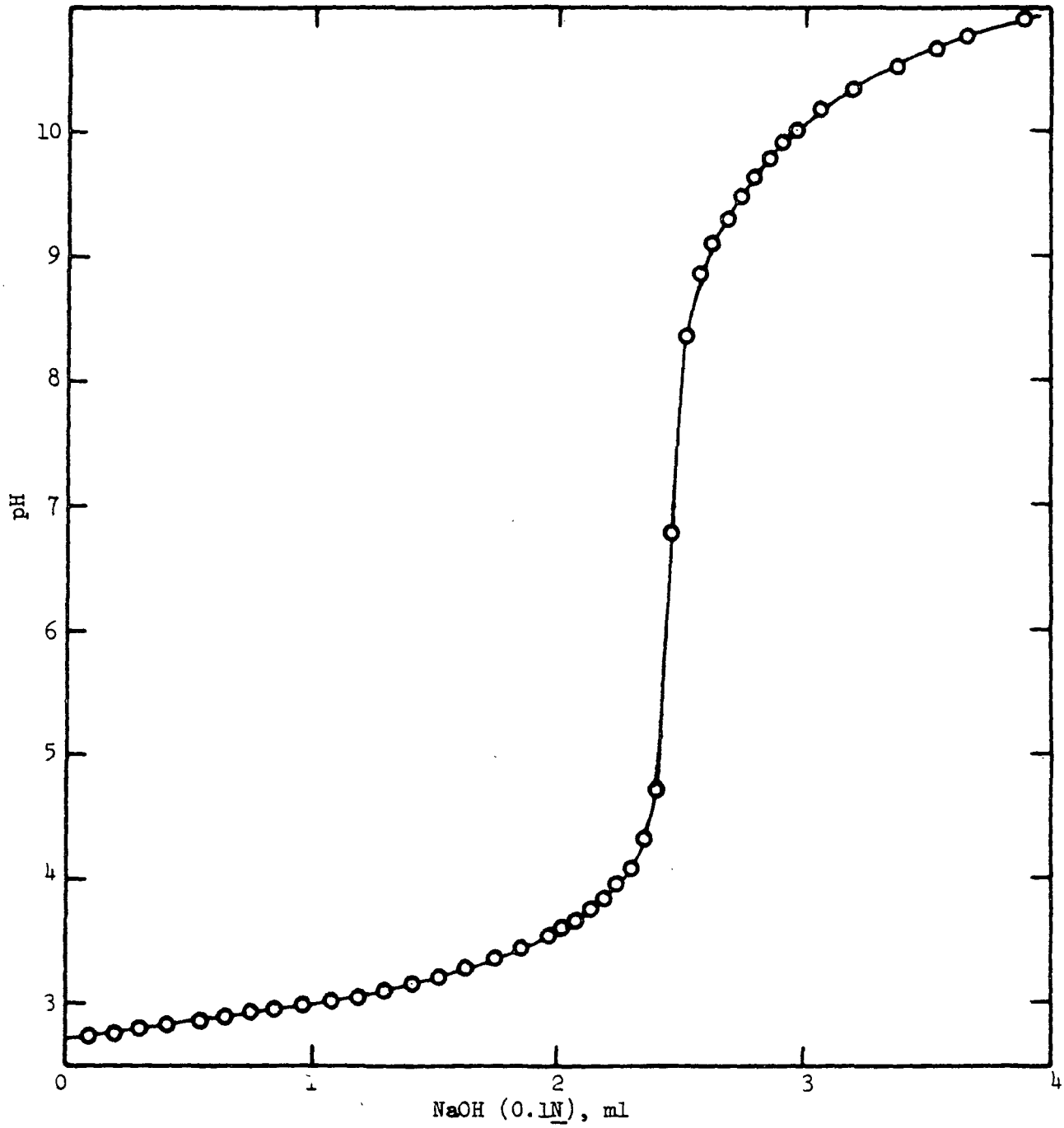

Figure 3. Potentiometric Titration Curve for Sample S-218 with no Added Salt

an equivalence point at a pH of 7. The fact that PSSA is a strong acid and is completely ionized has been shown previously by proton magnetic resonance (10).

Similar titrations were carried out with NaCl present at ionic strengths of 0.005, 0.048, and 0.55. Degrees of neutralization α were calculated from the equivalents of base added with complete neutralization ($\alpha = 1$) at pH equal to 7. The data are plotted in Fig. 4 as degree of neutralization against pH for the various ionic strengths. It is apparent that at pH's of interest to papermakers (>4), the polyacid is more than 90% neutralized.

The characterization studies show that we have produced a series of completely sulfonated, essentially monodisperse polyelectrolytes. They are strong acids which are virtually completely neutralized and ionized under the conditions of use. Because of this it is to be expected (11) that the chains will exist in a fairly extended state under conditions of low ionic strength. It has been argued (12) that such extension is favorable for bridging to occur between particles.

COMMERCIAL SAMPLES

Because only small quantities of the polystyrenes can be sulfonated with a justifiable amount of work, large-scale studies in the later stages of the project will be performed with commercially available samples of the polymer. These have broad molecular weight distribution and are 74-82% sulfonated. The particular samples to be used are the VERSA-TL series manufactured by National Starch and Chemical Corporation. The sample designations and the molecular weights given by the manufacturer are listed in Table II. Although these samples are not monodisperse, the effect of their widely differing molecular weights should be understandable on the basis of the bench-scale work where

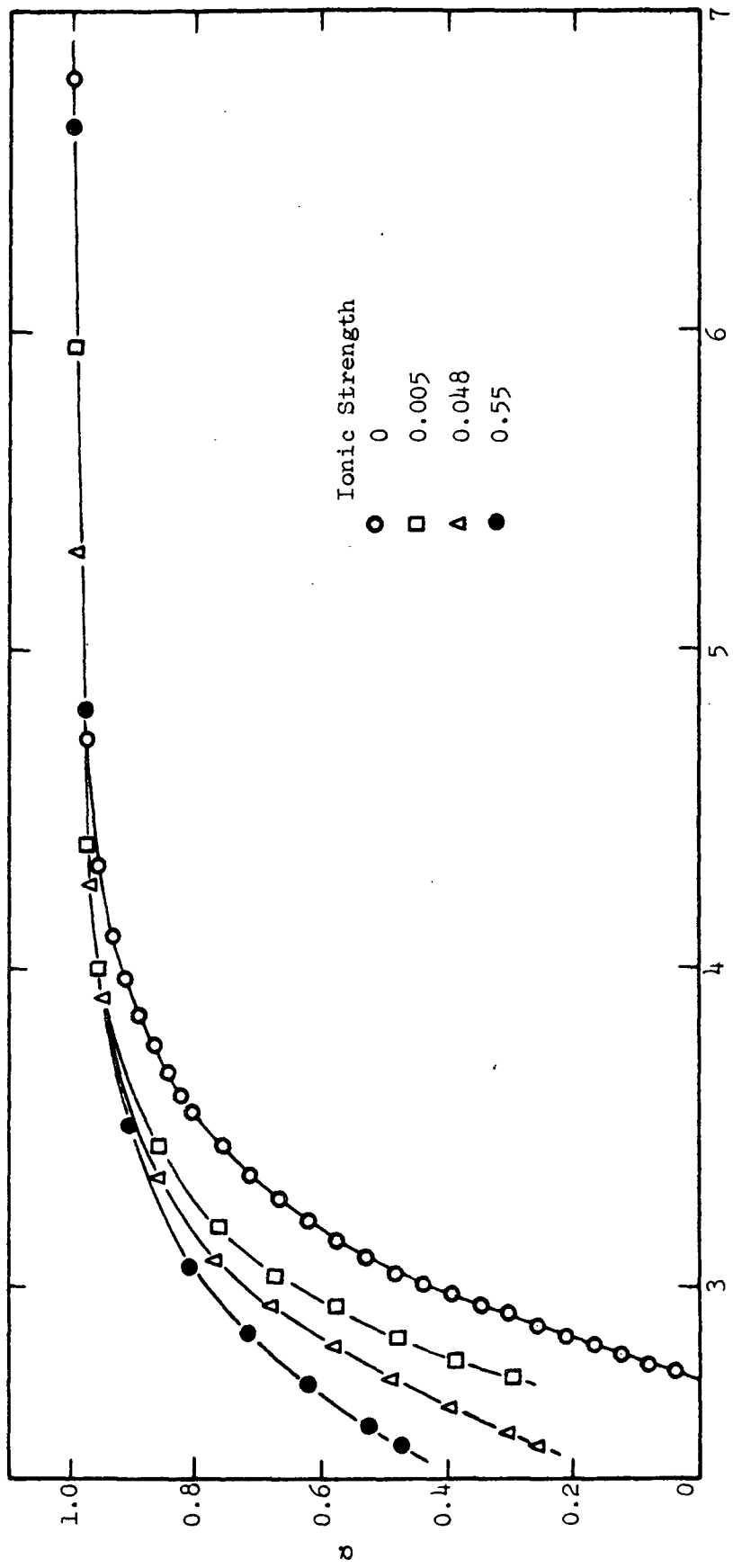

Figure 4. Degree of Neutralization α as a Function of pH at the Indicated Ionic Strengths of NaCl

the synthesized, monodisperse materials will be used. It is felt that because NaPSS is almost completely ionized under the conditions to be employed, the lack of complete sulfonation of the commercial samples will little affect their behavior as flocculants.

DETERMINATION OF NaPSS IN AQUEOUS SOLUTION

To follow the adsorption of NaPSS onto the particles to be flocculated, a means is necessary to measure the amount of the polymer left in solution. The substituted benzene ring offers a strong absorption hand in the ultraviolet region. According to Carroll and Eisenberg (6) the peak is at 225 nm. This was also found to be the case for the commercial samples and our synthesized materials. A linear relationship was found between absorbance at this wavelength and concentration of NaPSS up to at least 20 ppm polymer. This should encompass the useful range for flocculation and retention purposes.

MODEL PARTICLES

Titanium dioxide was chosen as the material to be flocculated or retained for a number of reasons. Its surface and electrokinetic properties have been previously studied in these laboratories (13). By a simple fractionation procedure a relatively narrow size distribution of particles can be obtained (14). Although it is expensive, TiO_2 is extensively used as a pigment and opacifier by the paper industry. Better retention would greatly improve the economics of its use.

PREPARATION

A 73% solids dispersion of RG-grade (The Glidden Company) titanium dioxide was prepared in accordance with previous work (13,14) by stirring in a malted milk mixer for 20 minutes. Cooling was provided to prevent excess heating and evaporation of water. The suspension was diluted to 7.5% solids and then stirred vigorously for two hours. Vacuum was applied to remove entrained air and the dispersion was allowed to settle for 24 hours. The fraction consisting of particles smaller than 1.0 μm was siphoned off the top of the partially settled suspension into a polyethylene bottle and was stored on a rotator to prevent settling and aggregation. Dilutions from this stock suspension (7.4% solids) were made for the subsequent flocculation and retention studies. The siphoning technique with the tip of the siphoning tube turned upward has been previously described (15). Suspension was drawn off to a depth determined by application of Stoke's sedimentation law.

$$h = (\rho_1 - \rho_2)d^2tg/18\eta$$

Here, h is the distance a particle of diameter d will fall in a time t under the acceleration of gravity g. The densities of the TiO_2 particles and

water are ρ_1 and ρ_2, respectively, and the viscosity of the latter is η. The distance a particle of TiO_2 with a diameter of 1.0 μm will fall in 24 hours is 14.3 cm and suspension was siphoned off down to this level.

CHARACTERIZATION

According to Webb (13) a suspension of this grade of titanium dioxide prepared as above will have a number average particle size of 0.130 μm and a weight average diameter of 0.152 μm. A fairly narrow distribution of sizes is indicated by these values and by the fact that 90% of the particles have diameters between 0.094 and 0.207 μm. He also found by electronmicrography that the particles were approximately spherical although with some surface roughness and that the specific surface area was 12.7 m^2/g. Since our material was prepared in the same manner, the same specific surface area will be assumed to hold.

ELECTROPHORETIC MOBILITY STUDIES

The electrophoretic mobility of a particle is a measure of its surface charge density and the ionic conditions in the near neighborhood. Adsorption of polymer or polyvalent ion or a change in the ionic strength of the system will produce concomitant changes in the electrophoretic mobility. It is often said that when this parameter is zero, the optimum conditions for flocculation or retention obtain. This is certainly not always the case because other factors may come into play in a given system, but it is probably safe to say that a relatively low value of the electrophoretic mobility is conducive to good flocculation.

In the present study we are interested in relating the electrokinetic properties to the adsorption of polymer and the degree of flocculation. A number of experiments were carried out on the Numinco Electrophoretic Mass Transport analyzer. This instrument works on the principle (16) that electrically charged particles are physically transported toward the oppositely charged electrode when an electric field is imposed on the system. The weight of the suspension in a small collection chamber connected by a small opening to a large reservoir filled with the same suspension is measured before and after the passage of a known quantity of electricity through the system. The change in weight can be related to the electrophoretic mobility. The results were, in general, disappointing. Webb (13) was able to achieve reproducible results while working at about 7% solids. Our studies were performed at 0.76% TiO_2 and with various amounts of added polymers and simple salts. At even this concentration of TiO_2 (which is far greater than that encountered in a paper furnish or white water) the amount of material transported was too small to measure reproducibly. It must be concluded that this instrument is incapable of giving useful results for this project.

More recently we have had the opportunity to make a few measurements of the electrophoretic mobility on a Laser Zee Meter (Pen Kem Company) (17). This instrument uses basically the microelectrophoresis technique (16) whereby the particles in the applied electric field are viewed through a microscope and their velocity determined. Measurements were made on suspensions with concentrations of TiO_2 between 10 and 125 ppm and with various polymer additives. Reproducibility was excellent. This instrument may be useful for the interpretation and understanding of the phenomena occurring during flocculation. Detailed studies of the effect of various amounts of polymeric flocculant and simple

electrolyte on the electrophoretic mobility must await our possible acquisition of this instrument.

PULP FIBERS

For the retention studies a large stock of beaten pulp was made up. A bleached softwood kraft was beaten to a Canadian freeness of 400 cc in a Valley beater at 2% consistency. Several 5-pound batches were beaten, dewatered, shredded, and mixed thoroughly. Formaldehyde at a concentration of 0.5% on the weight of dry fiber was mixed in to prevent bacterial growth during storage. The total of 22.2 pounds (ovendry) of beaten pulp was stored at 28% solids in a cold room at 5°C. Past experience has shown that the freeness of pulp stored under these conditions changes only slightly with time and negligibly after about a month of storage.

FUTURE WORK

At present, work on the project is continuing along two parallel tracks. In the first the flocculation of the TiO_2 particles by the polymeric flocculant is being studied. The important parameters here are the molecular weight and concentration of the flocculant, the ionic strength of the suspension, and the mixing time before allowing the floc to settle. The second set of experiments is concerned with the stability of the formed floc to subsequent hydrodynamic shearing. The laminar flow region will be examined first by using a counterrotating couette viscometer to obtain well-defined shearing stresses.

Subsequent studies will deal with the retention of TiO_2 on pulp fibers. Handsheet experiments will be followed by sheet formation on the dynamic drainage tester (18). This latter apparatus has a constant rate of drainage and is capable of covering the drainage rates obtaining on most paper machines. In these studies the concentration and molecular weight of the polymer retention aid and the ionic strength of the furnish will be major variables. In addition, the sheets formed on the handsheet mold and in the dynamic drainage tester will be monitored for opacity, formation, and strength as well as overall retention. These experiments should provide the necessary data for a better understanding of the flocculation and retention processes.

ACKNOWLEDGMENTS

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